7.—THE ESSENTIAL OILS OF THE WESTERN AUSTRALIAN EUCALYPTS.

PART V.

THE OILS OF *E. ASTRINGENS*, MAIDEN, AND *E. PYRIFORMIS*, TURCZ.

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EUCALYPTUS ASTRINGENS.

E. astringens, the brown mallet, is confined to the south-western portion of Western Australia, occurring in areas up to 100 acres in extent over country within the 12-inch to 25-inch rainfall belt. It extends from York to as far south as Cranbrook on the Great Southern Railway, westwards to Wandering and Arthur and eastwards to beyond Ravensthorpe.

The true wood of the tree varies in colour from light red-brown to a dark grey-brown; it has a fine and uniform texture and is very dense. Langlands (1937) has shown that the wood should be superior to that of the Queensland spotted gum (*E. maculata*) and karri (*E. diversicolor*) for such purposes as tool handles and that it should prove a satisfactory substitute for hickory for all but the most exacting purposes.

The bark is smooth, brown or bronze in colour and easily stripped from the tree throughout the greater part of the year. It varies in thickness from ¼-inch to ¾-inch, and it has a ready market on account of its high tannin content. The amount of bark stripped during the year July, 1936, to June, 1937, was 2,119 tons, of which 1,425 tons, valued at £14,491, was exported.

The leaves are shining, dark green in colour, lanceolate, and are freely dotted with oil glands. The veins are widely spaced and somewhat irregular; the marginal vein, which is well removed from the edge of the leaf, is indented to meet the lateral veins.

In view of the economic importance of the bark and of the valuable properties of the wood, additional interest attaches to the nature and possible uses of the oil.

The material used in this investigation was obtained through the courtesy of Mr. W. G. Chandler, B.Sc. (For.), Dip. For. (Canberra), of the Forests Department. It was collected during the flowering season, mid-October, in the vicinity of Narrogin, and its identity was verified by Mr. C. A. Gardner, Government Botanist.

The oil, which distilled rapidly, was pale greenish-yellow in colour, and had a pleasant, non-irritating smell. The yield was not high, varying from 0.5 to 0.6 per cent. calculated on air-dried material. The cineol content averaged nearly 50 per cent., and pinene was present in appreciable amount. The free acid and ester contents were small; alcohols, calculated as geraniol, made up little more than 8 per cent., and both low and high boiling aldehydes were present in small amount. The usual colour reactions for aromadendrene were given, and the oil slowly developed a purple colour when treated with ferric chloride. Phellandrene was absent. On distillation, insoluble material separated as boiling commenced; 81 per cent. of the oil was volatile below 195°, the rectified oil containing only little more than 60 per cent. of cineol. The oil is therefore of little value as a medicinal oil and it does not appear likely to be of any mining value.

EUCALYPTUS PYRIFORMIS.

E. pyriformis is a small shrub or mallee with long, weak and straggling stems up to 15 feet in height. It is widely distributed in Western and South Australia, occurring, in this State, between the Murchison and Moore Rivers, at least as far west as Coorow and south-east to Tammin; its eastern limit does not appear to have been defined.

The wood is pale brown in colour, and the bark light brown and smooth. The leaves are large and broadly lanceolate, being up to nearly 6 inches long and nearly 2 inches wide; the surface is subglaucous, the lamina freely dotted with oil glands and the venation that of the cineol-pinene type.

The material used in this investigation was collected by Mr. John Baxter towards the end of May, 1937. It was obtained from typical specimens in an area about 11 miles east of Marchagee, and was identified by Mr. G. R. W. Meadly, Assistant Government Botanist.

The oil, which distilled completely in from 4 to 5 hours, was pale yellow in colour and had a pleasant, non-irritating smell similar to that of the cineol-pinene oils. Its solubility in alcohol was low and it contained an appreciable amount of pinene, more than 14 per cent. of the oil distilling below 164°. The cineol content was 56 per cent. Esters were present in small amount and they were practically all low boiling; geranyl acetate was present in traces only. Both low- and high-boiling aldehydes were present, and the oil contained, in addition, aromadendrene and a small amount of a substance giving a purple colour with ferric chloride. The saponification values of the acetylated oil indicated that alcohols other than geraniol were present, and an appreciable amount of crystalline eudesmol was separated from the oil on redistillation. Fractionation of the oil showed that little more than 80 per cent. was volatile below 195° at ordinary pressure; the cineol content of this rectified oil was approximately 70 per cent. The separation of insoluble matter was again noted as boiling commenced.

EXPERIMENTAL.

EUCALYPTUS ASTRINGENS.

The dried oil had the following properties (physical properties given at 20°):—Specific gravity, 0.911; refractive index, 1.469; specific rotation, +7.3°; soluble in 1.1 volumes of 80 per cent. alcohol; acid value, 1.0; saponification values: hot 8.0, cold 5.0; saponification values of the acetylated oil: hot 38.7, cold 27.6, the latter corresponding to 6.2 per cent. of alcohols calculated as geraniol; cineol, 49.5 per cent.; aldehydes, 0.054 milligram mol per gram of oil.

On redistillation, the following fractions were obtained:—

Fraction.	Boiling Range.	Amount.	Specific Gravity.	Refractive Index.	Specific Rotation.
1.	Up to 165° ..	22.2 per cent.	0.894	1.464	+22.2°
2.	165—180° ..	49.7 per cent.	0.905	1.464	+ 9.6°
3.	180—195° ..	9.2 per cent.	0.928	1.468	— 7.1°

The residue (18.9 per cent.) was further distilled under reduced pressure.

4.	90—105°/26mm.	2.1 per cent.	0.948	1.482	—19.4°
5.	105—130°/25mm.	3.7 per cent.	0.953	1.495	—18.3°
6.	130—155°/24mm.	5.5 per cent.	0.945	1.500	— 2.3°
7.	155—168°/24mm.	4.7 per cent.	0.970	1.503	— 4.3°

From the residue, 9.65 per cent. of white solid was separated by adding ether and filtering.

Fraction 1 was yellow in colour, acidic, and contained volatile aldehydes. Pinene was present in quantity and was isolated as its nitrosochloride.

Fraction 2 was pale yellow in colour and contained a little over 60 per cent. of cineol. Its cold and hot saponification values were 7.6 and 11.6 respectively, whilst the corresponding values for the acetylated oil were 25 and 29. It contained a trace of aldehyde.

Fraction 3 was colourless and contained 71 per cent. of cineol; its hot saponification value was 5 and the corresponding figure for the acetylated oil was 87. It contained no aldehyde.

Fraction 4 was colourless, contained no aldehydes and gave no colouration with ferric chloride.

Aldehydes were present in the last three fractions, with maximum amount in fraction 6. Aromadendrene was present in greatest amount in fractions 5 and 6. With ferric chloride, a trace of olive green colour was obtained with fraction 6, and a purple colour with fraction 7.

EUCALYPTUS PYRIFORMIS.

The oil was obtained in from 1.0 to 1.1 per cent. yield, and, after drying, it had the following properties:—Specific gravity, 0.920; refractive index, 1.469; specific rotation, +8.4°; soluble in 1 volume of 80 per cent. alcohol; acid value, 0.65; ester value: cold, less than 0.1, hot, 3.35; saponification values of acetylated oil: cold 30.6, hot 56.7, the former corresponding to 8.3 per cent. of alcohols calculated as geraniol, and the difference corresponding to 8.8 per cent. of alcohols calculated as eudesmol; cineol, 56 per cent.; aldehydes, 0.04 milligram mol per gram of oil. The oil gave the usual colour reactions for aromadendrene and gave, slowly, a purple colouration with ferric chloride.

On redistillation, the following fractions were separated:—

Fraction.	Boiling Range.	Amount.	Specific Gravity.	Refractive Index.	Specific Rotation.
1.	Up to 164°	14.6 per cent.	0.890	1.463	+22.2°
2.	164—170° ..	30.2 per cent.	0.901	1.463	+14.4°
3.	170—179° ..	31.2 per cent.	0.920	1.462	+ 2.5°

The residue (24 per cent.) was further fractionated under reduced pressure:—

4.	85—190°/20mm.	5.6 per cent.	0.939	1.470	..
5.	100—125°/19mm.	3.9 per cent.	0.962	1.490	..
6.	125—150°/19mm.	3.2 per cent.	0.962	1.496	..
7.	150—165°/19mm.	7.2 per cent.	..	1.505	..

From the residue, 0.77 per cent. of insoluble material was separated by addition of ether and filtering.

Fraction 1 was practically colourless and contained a considerable quantity of *d*-pinene which was readily isolated as its nitrosochloride. It was strongly acidic and contained, in addition, cineol and a small amount of volatile aldehyde.

Fraction 2 was colourless and also contained an appreciable amount of *d*-pinene. With fraction 3, it contained practically the whole of the esters present in the oil. The cineol content was nearly 60 per cent. and aldehydes were present in traces.

Fraction 3 contained 80 per cent. of cineol, had a saponification value of 7.1, and contained a trace of aldehyde. Fraction 4 was similar, although the cineol content was lower.

Fractions 5, 6 and 7 all contained aromadendrene (maximum amounts in fractions 5 and 6) and high boiling aldehyde (maximum in fraction 6).

Fraction 7 was pale yellow in colour and gave a purple colour with ferric chloride. It solidified on standing, and from the solid material crystalline eudesmol (m.p. 79°) was separated in quantity.

The authors are indebted to Mr. W. G. Chandler and Mr. J. Baxter for the collection, and to Mr. C. A. Gardner and Mr. G. R. W. Meadly for the identification of material.

Reference:

1937: Langlands—Properties of Australian Timbers, Part 2—Brown Mallet (*E. astringens*). *Coun. Sci. Ind. Res.* (*Aust.*), Pamphlet 73.

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